

# PATENT SPECIFICATION

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DRAWINGS ATTACHED

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## (54) MODIFIED KAOLIN CLAYS

(71) We, GEORGIA KAOLIN COMPANY, a corporation organised and existing under the laws of New Jersey, United States of America, of 433 North Broad Street, Elizabeth, New Jersey 07207, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to surface modified kaolin clays and methods of making them. Throughout the present specification, the term "kaolin clay" is used to mean kaolinite, halloysite, dickite, nacrite or anauxite.

Kaolin clays in their naturally occurring state are hydrophilic and, consequently, difficulties are often experienced in incorporating such clays into organic polymer systems. In addition, the hydrophilic nature of the kaolin surface presents difficulties in compounding plastics compositions, since water is more readily adsorbed on to the hydrophilic surface than is often desirable. Numerous methods have been described in the literature for the modification of the kaolin surface with organic materials so as to convert the naturally hydrophilic surface into one with organophilic properties. In particular, the modification of the kaolin surface with derivatives, and particularly salts, of organic amines has been described, and the properties resulting from this treatment have been claimed to give advantageous properties to polyesters, to elastomers, and to plastics. Typical of such prior art practices are those disclosed in U.S. Patents Nos. 2,999,080; 3,032,431; and 2,948,632.

The methods which have been described rely on the fact that kaolin possesses, at or near its surface, inorganic cations which can be exchanged for organic cations. Thus, the reaction is termed a cation exchange

reaction and involves the cations of the organic material interchanging with the inorganic cations, which are naturally present on the kaolin surface.

We have found that treatment of a dry kaolin clay with an organic amine (which term is used herein to include urea) under anhydrous conditions, in an anhydrous organic solvent, results in organic modified clays with unique and desirable properties. The treatment provides clays which are particularly suitable fillers for polyesters, polyurethanes, rubbers, polyvinyl chloride, and polyethylene. This technique of modifying the clay surface with organic amines is distinguished from those known by the following features:

1. It does not involve directly, nor is it limited by, the base exchange capacity of the mineral.
2. The cations present on the mineral surface, either in the natural state or as a result of subsequent treatments, are not displaced by the organic amine.
3. The bond formed between the amine and the kaolin surface is strong and more resistant to degradation than the known products.

Many organic solvents are satisfactory for carrying out the treatment of this invention provided they fulfill the requirement of being anhydrous. Solvents typical of those used in this invention are:

1. trichloroethylene
2. carbon tetrachloride
3. benzene and members of the homologous aromatic series
4. esters
5. nitroparaffins
6. nitroaromatics

7. ethers
8. ketones
9. petroleum ether and higher members of this series and any solvent containing as substituents groups which are less polar than an organic amine

Of particular value is the use of trichloroethylene because of its non-polar and non-toxic characteristics. Petroleum fractions are also usable.

In general, we have found that the lower the water content of the clay surface the better the product formed on treatment with the organic amine. But compromises can be reached; for example, where the water content approaches 1%, satisfactory organic modified kaolins can be prepared if the amount of organic amine is increased above the optimum level for the fully dried clay. Thus, in some situations, it may be commercially desirable to sacrifice slightly the technical improvement resulting from completely drying the clay because of the easier production requirements to be found in the use of the partially dried clay. Preferably, the surface water content of the clay is less than 1% by weight, and advantageously less than 0.7% by weight, as measured at 110°C.

The amount of amine required to modify the surface also varies with the end use for which the clay is being prepared. In general, amine treatments of up to 2% can be used, but no general rules can be laid down for any given optimum concentration of amine. When the amine is monomeric, it is preferably used in an amount of not more than 1% by weight of the clay, advantageously in an amount of from 0.2 to 0.6% by weight of the clay. With polymeric amines, greater amounts are normally used.

In general, a wide range of amines has proven satisfactory for use in this process, preferably they are of the general formula  $N(R)(R_1)(R_2)$  in which R and  $R_1$ , which may be the same or different, are alkyl or hydrogen and  $R_2$  is an optionally-substituted alkyl group. The term "optionally-substituted alkyl group" is used herein to mean that the alkyl groups may if desired, be substituted by one or more functional groups. Suitable functional groups are, for example, such substituents as ester or aryl groups, and also further amino groups or carbon-carbon double bonds. The amine can be, for example, a polymer containing free amino groups or can be a monomer containing groups capable of polymerisation and which can be used to form a polymeric coating on the clay surface. It is necessary that the amino groups form the most polar part(s) of the molecule in order to assist adsorption on the clay.

The selection of the amine treatment required for a kaolin can be governed to some extent by the type of polymer to be used in the final fabrication. The effect of various amines on viscosity is shown in the accompanying drawing, given by way of illustration only, in which:

Figure 1 is a graph of viscosity versus amine chain length in polyester;

Figure 2 is a graph of viscosity versus amine chain length in mineral oil.

Referring to the drawings, with the relatively polar polyester-type compositions, viscosity of a series of amines which differ in the carbon chain lengths is shown in Figure 1, where it can be seen that the optimum viscosity is reached with 4 to 8 carbon atoms in the chain, while the minimum viscosity is reached with 6 to 8 carbon atoms in the chain. On the other hand, mineral oil viscosities show a gradual decrease with increasing chain length as shown in Figure 2. This is a situation somewhat similar to that to be expected in rubber and similar non-polar polymers. The products of this invention give much better dispersion in e.g. polyesters and mineral oil than the products of the prior art.

The precise theoretical reasons for the success of the above treatment have not been fully established, but it has been shown that surface acidity increases with a decrease in the water content of the clay surface; and this is a possible explanation for the treatments described. It should be noted that since these treatments do not involve directly the cations present naturally on the clay surface, the products will differ significantly from those of the prior art. It is likely, although not necessary, that interaction involves the crystal edges and the strong acid sites developed on these clays on drying.

The precise level of amine treatment required varies with the surface area and particle size of the kaolin used. In general terms, the larger the surface area and the smaller the particle size, the greater the amount of amine required to achieve the desirable treatment.

As stated above, the amine treatment is also a function of the water content and at increased water contents up to 1%, increased amine levels are normally used.

When the amine contains substituent groups capable of polymerisation, it is desirable to further modify the clay by treatment with a free-radical initiator, such as an organic hydroperoxide, a peroxide, or a compound containing azo groups. Such further treatment appears to polymerise the amine and form a polymeric surface coating. It is also possible to treat the amine-coated clay with formaldehyde, and this

also can result in the formation of a polymeric coating on the clay.

In order that the invention may be more fully understood, the following Examples are given by way of illustration only. In the Examples, each of the clay samples were dry, furthermore, each of the organic diluents were anhydrous.

#### EXAMPLE I

This example illustrates the influence of the amount of residual water of the kaolin on the effectiveness of the amine treatment. A processed kaolin with average particle size 0.55 micron was dried and samples removed which had a residual water con-

tent of 0.0, 0.5, 0.75, and 1%. Each of these clays was then slurried in trichloroethylene so that the solids content was approximately 20%. To each of these slurries, hexylamine was added incrementally until optimum dispersion resulted.

The amount of hexylamine required for each clay is shown in Table I. It can readily be seen that the drier the clay, the lower the amine content required for dispersion. Furthermore, tests on the hydrophobic nature of these clays show that the modified clay made from the dried kaolin, that is, sample 1, was much more hydrophobic than where the initial clay contained 1% moisture.

TABLE I  
Relationship Between Residual Water Content of Clay\* and Amount of Amine Required

Sample No.	Water Content of Clay**	For Dispersion+
		Wt. % Hexylamine Required for Dispersion in Trichloroethylene
4	1%	2.0%
3	0.75%	1.0%
2	0.5%	0.8%
1	0.0%	0.5%

\* The clay used for these experiments was a processed clay, i.e. deagglomerated and deflocculated.

\*\* As measured at 110°C.

+ These experiments were conducted at 20 wt % clay in trichloroethylene

The test for hydrophobicity was carried out by sprinkling the modified clay onto the surface of water and observing the time taken for the water to wet the organic clay complex.

Similarly, where the amine used to modify the clay was butylamine, the results shown

in Table II were obtained and where octadecylamine was used, the results shown in Table III were found.

When a product is obtained by conventional cationic exchange methods, it is much more readily wetted by water.

#### EXAMPLE I

TABLE II  
Relationship Between Residual Water Content of Clay and the Amount of Butylamine Required for Dispersion

Sample No.	Water Content of Clay (approx.)	Amount of Butylamine Required for Dispersion in Trichloroethylene
1	1.0%	1.5%—2.0%
2	0.75%	1%
3	0.50%	1%
4	0.0%	0.5%

TABLE III  
Relationship Between Residual Water Content of Clay and the Amount of Octadecylamine Required for Dispersion

5	Sample No.	Water Content of Clay (approx.)	Amount of Octadecylamine Required for Dispersion in Trichloroethylene
10	1	1.0%	0.8%
	2	0.75%	0.5%
	3	0.50%	0.5%
	4	0.0%	0.1%—0.2%

#### EXAMPLE II

15 This example illustrates the influence of the carbon chain length of primary amines on the properties of the clay. Primary aliphatic amines with carbon chains from 4 up to 18 carbon atoms were used to modify a dried, processed kaolin with average particle size 0.55 micron. The general treatment conditions were those described in Example I, that is, the clay was slurried in trichloroethylene to which had previously been added the amine. After stirring for 20 30 minutes, the clay was removed by filtration and dried. The viscosities of these treated clays in a polyester resin<sup>o</sup> and in mineral oil<sup>=</sup> are shown in Figures 1 and 2.

25 It should be noted that the polyester resin used was "Selectron" (trade mark) 5067\* and the mineral oil was a paraffin grade hydrocarbon, sold under the trade name Primol 355 by Humble Oil Company. The polyester viscosity represents a moderately polar organic system and the mineral oil a non-polar system which has a similarity to rubber in properties. The viscosities shown in the Figures clearly indicate that in the polyester system optimum viscosity is obtained with the carbon chain length of between 4 and 8 carbons, whereas in rubber the higher the chain length or the longer the chain length the more desirable the treatment.

45 This is shown by the lower viscosity given with the higher chain length amine modified clays. These clays are particularly

noted for their high bulking value, which again is an indication of the extremely good dispersion obtained by this process. When compared with products made by the prior art, it is found that the bulking value is generally about 60—70% that of the untreated clay and this is a clear indication of the effectiveness of this treatment procedure. 60 65

#### EXAMPLE III

This example illustrates the use of a secondary amine as the modifying agent for the clay. The amine modified clay was prepared as described in Example II. The secondary amine used was dioctylamine at 1% wt. of clay. The properties were as follows: 70

viscosity in polyester, 34,000 cps. 75  
viscosity in mineral oil, 12,000 cps.

#### EXAMPLE IV

This example illustrates the use of a tertiary amine as the modifying agent. A clay was treated as described in Example I with dimethyloctadecylamine and gave the following properties: 80

viscosity in polyester, 86,500 cps.  
viscosity in mineral oil, 3,400 cps.

#### EXAMPLE V

85 This illustrates the use of amines which can subsequently undergo reaction and resin formation with other compounds. A dried clay of average particle size, 0.55 micron, was slurried in trichloroethylene so as to give a 20% solids slurry. To this slurry was added melamine (5% by weight of the clay) and then after 30 minutes a solution of paraform (same wt. as melamine) in butanol. 90 95

The reaction was allowed to proceed for a further 30 minutes to produce a melamine formaldehyde coating on the clay surface.

\* Supplied by Pittsburgh Plate Glass Co.

50 <sup>o</sup> Viscosities were measured at 10 r.p.m. with spindle No. 5 on a Brookfield Viscometer. 40 pts. of treated clay were mixed with 60 pts. of polyester resin.

55 <sup>=</sup> Viscosities were measured at 10 r.p.m. with spindle No. 5 on a Brookfield Viscometer. 20 pts. of treated clay were mixed with 80 pts. of mineral oil.

Similarly, the use of urea in place of the melamine gave a clay which could be converted to a urea formaldehyde product. It was also noted that the melamine clay adduct and the urea clay adduct could be used successfully without the formaldehyde modification as fillers in molding phenolic melamine and urea formaldehyde resins.

#### EXAMPLE VI

This illustrates the use of amines containing groups capable of undergoing vinyl polymerization. Modification of the clay was as described in Example I using vinyl pyridine, 5-methyl 2-vinyl pyridine, dimethylaminoethyl methacrylate, tertiary butylaminoethyl methacrylate. The properties of these modified clays are as listed below.

#### Properties of Treated Clay

Sample No.	Viscosity in Polyester	Viscosity in Mineral Oil
1 — Vinyl pyridine ... ..	7,000	33,000
2 — 2-Methyl 5-vinyl pyridine ...	6,000	32,000
3 — Dimethylaminoethyl methacrylate	4,000	28,000
4 — Tert.butylaminoethyl methacrylate	10,000	14,000

The properties of the treated clays produced in this Example were evaluated by compounding in the following rubber composition:

Plioflex (trade mark) SBR 1502	75.0 pts.
Clay filler ... ..	39.0 pts.
Zinc oxide ... ..	3.75 pts.
Coumarone resin ... ..	5.64 pts.
Sulphur ... ..	2.26 pts.

"Santocure" (trade mark, marketed by Monsanto) ... .. 1.50 pts.  
The rubber compositions were compounded on a two-roll mill and then cured.

The treated clays were much more readily incorporated into the rubber than the untreated clay, as shown by the time for dispersion:

Untreated clays ... ..	25 minutes
Clay (Sample 3) (dimethylaminoethyl methacrylate) ... ..	10—15 minutes
Clay (Sample 4) (tert.butylaminoethyl methacrylate) ... ..	10—15 minutes

When the rubber compositions were cured for 10 minutes at 160°C., the following properties were given by the rubbers:

Filler	Shore Hardness (after 72 hours)
Untreated clay ... ..	59
Clay (Sample 3) ... ..	64
Clay (Sample 4) ... ..	64

#### EXAMPLE VII

The modified clays as prepared in Example VI were further treated with 1% by weight of an organic peroxide or hydroperoxide and then used as the filler in rubbers or in polyesters. Greatly improved mechanical properties resulted and this suggests that polymerization from the surface and involving the amine residue had taken place.

#### Results

Modifying Amine (1% on Clay)	Properties of Rubber* Shore Hardness (after 72 hrs.)
Dimethylaminoethyl methacrylate + Cumene hydroperoxide (1% on clay) ... ..	64
Tert.butylaminoethyl methacrylate + Cumene hydroperoxide (1% on clay) ... ..	64
Untreated clay ... ..	59

\* Rubber composition used was as in Example VI.

## EXAMPLE VIII

This example illustrates the use of polymers which contain free amino groups as the modifying agent for the clay in place of the simple primary, secondary, and tertiary amines described above. The treated clays were incorporated into polyesters ("Versamids"—marketed by General Mills—Versamid is a trade mark), and gave the properties shown below.

Properties of "Versamid"*		Modified Clay
Viscosity in Polyester	...	6500
Viscosity in Mineral Oil	...	4000

The milling time of this modified clay under conditions used was 10 minutes. Untreated required 30 minutes.

\* "Versamid" 140 was used.

## Properties of Rubber Mixes

	Shore Hardness
Untreated clay	59
"Versamid" 140 modified clay	64

Similarly, when an acrylic polymer with a composition of tert.butylaminoethyl methacrylate/methyl methacrylate=70/30 and M. wt. 40,000 was used, the treated clay had the following properties:

No heat treatment — polyester viscosity 4,000 at 10 RPM  
After heating 1/2 hour at 80°C. — polyester viscosity 4,400 at 10 RPM

Once again the sample with the subsequent heat treatment was more hydrophobic than the untreated melamine formaldehyde-clay product.

## EXAMPLE IX

This example illustrates the use of different solvents for the treatment of the clay with the amine. A clay with the particle size dimensions of 0.55  $\mu$  was slurried in each of the following solvents:

carbon tetrachloride  
trichloroethylene  
petroleum ether fraction  
boiling point 40 to 60  
petroleum ether fraction  
boiling point 80 to 100  
benzene  
toluene

In each case, the clay was modified by treatment with 1% by weight of hexylamine. After the modified clay had been removed

Viscosity in Polyester = 4000  
Viscosity in Mineral Oil = 4800

## EXAMPLE VIIIa

A dried clay was treated with a urea formaldehyde\* resin as described in Example I. Two types of treatments were used: First the urea-formaldehyde resin was adsorbed onto the clay and the product isolated in the normal manner. The results obtained were as follows:

Wt. % Urea Formaldehyde on Solid Basis	Viscosity Polyester	Spindle No. 6)
1%	11,200	
2.5%	4,400	

\* F 240 N supplied by Rohm & Haas Company

In the second method, the slurry, after adding the urea formaldehyde resin, was heated with stirring for 1/2 hour at 80°C. A clay treated in this manner with 5% urea-formaldehyde resin gave a polyester viscosity of 8800 (Spindle No. 6). This clay was much more hydrophobic than a similar material prepared without the subsequent heat treatment.

Similarly, when a melamine formaldehyde resin (MM 55 HV, supplied by Rohm & Haas) was used at 5% by weight, the results were as follows:

by filtration and dried, a comparison of the viscosities of these clays in polyester and in mineral oil showed no significant differences between the various treatments.

## EXAMPLE X

This example illustrates the use of clays which have been subjected to different pretreatments. A naturally occurring kaolinite, a kaolinite prepared by blunging, bleach and then acid precipitation, a predispersed kaolinite, and delaminated kaolinite were each modified by the process described above. A comparison of the original clay and the modified clay showed that in all cases the amine modification resulted in a greatly improved hydrophobic surface.

## WHAT WE CLAIM IS:—

1. A process for modifying kaolin clays, 100

- as herein defined, which comprises treating a dry kaolin clay with an organic amine (as hereinbefore defined) under anhydrous conditions in an anhydrous organic diluent.
- 5 2. A process according to claim 1, in which the surface water content of the clay is less than 0.7% by weight, as measured at 110°C.
- 10 3. A process according to claim 2, in which the surface water content of the clay is less than 0.7% by weight, measured at 110°C.
- 15 4. A process according to any of claims 1 to 3, in which the organic amine is monomeric and is used in an amount of not more than 1% by weight of the clay.
- 20 5. A process according to claim 4, in which the amine is used in an amount of from 0.2 to 0.6% by weight of the clay.
- 25 6. A process according to any of claims 1 to 5, in which the organic amine is of the formula  $N(R)(R_1)(R_2)$  in which R and  $R_1$ , which may be the same or different, are an alkyl group or a hydrogen atom, and  $R_2$  is an optionally-substituted alkyl group (as herein defined).
- 30 7. A process according to claim 6, in which  $R_2$  is substituted by one or more carbon-carbon double bonds and/or further amino groups.
8. A process according to any of claims 1 to 7, in which the organic amine is a polymer containing free amino groups.
9. A process according to any of claims 1 to 8, in which the amine-treated clay is further modified by treatment with an organic free radical initiator.
10. A process according to claim 9, in which the free radical initiator is an organic hydroperoxide, a peroxide or a compound containing an azo group.
11. A process according to any of claims 1 to 10, in which the amine-treated clay is further modified by treatment with formaldehyde.
12. A process for modifying kaolin clays substantially as herein described in any of the Examples.
13. A modified kaolin clay produced by the process claimed in any of the preceding claims.
14. An amine modified clay which comprises a kaolin clay having an amine bonded to the surface thereof independently of ion exchange sites on said surface.
15. A polymer comprising having as a filler therein a modified kaolin clay as claimed in claim 13 or 14.

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Fig. 1.

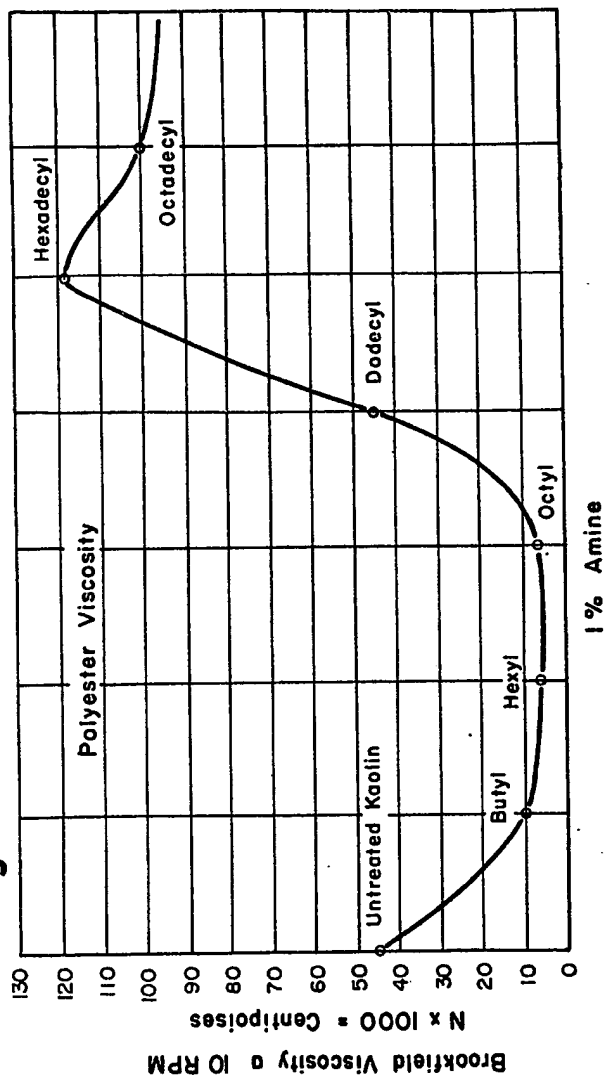


Fig. 2.

